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## СПЕКТРОСКОПИЯ ТВЕРДОГО ТЕЛА

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# Size Effects in Triplet-Triplet Annihilation. I. Standard and Statistical Approaches

© 2005 г. M. N. Berberan-Santos*, E. N. Bodunov**, and J. M. G. Martinho*
*Centro de Quimica-Fisica Molecular, Instituto Superior Tecnico, 1049-001 Lisboa, Portugal
**Petersburg State Transport University, Physical Department, 190031 St. Petersburg, Russia
E-mail: bodunov@mail.admiral.ru

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**Abstract**—The dynamics of triplet-triplet annihilation is theoretically studied in linear chains and nanoparticles as a function of size, $M$, the rate of excitation migration, $W$, and the rate of excitation annihilation, $V$. It is shown that a sum of two exponentials is usually sufficient for fitting experimental phosphorescence and triplet-triplet absorption decays. The first term describes the decay of domains containing initially one triplet, while the second one reflects the disappearance of domains containing initially two triplets.

## 1. INTRODUCTION

Size and topology of multichromophoric nanosystems critically affect their spectral properties, as well as excited state time and space evolution. In particular, singlet excitation energy migration and trapping have been studied in detail in multichromophoric rings [1], linear chain polymers [2, 3], small regular lattices [4], dendrimers [5, 6], and photosynthetic systems [7]. Recently, attention was also paid to multiphoton processes in nanosystems, including singlet-singlet annihilation [8–10] and triplet-triplet annihilation (TTA) [11, 12].

Triplet-triplet annihilation is an important process that strongly influences the optical and optoelectronic properties of a multitude of systems at relatively high excitation intensities, like homogeneous liquid solutions [13, 14], micellar solutions [11], molecular crystals [15], polymers [12, 16, 17] and Langmuir–Blodgett films [18].

TTA corresponds to the energy transfer process $T_1 + T_1 \longrightarrow S_1 + S_0$, whereby two excited molecules in the lowest triplet state yield, upon close proximity, a ground state molecule and an excited molecule in the singlet state [19]. Several processes can then follow, namely unimolecular ones, $S_1 \longrightarrow S_0$ (including delayed fluorescence and internal conversion), and $S_1 \longrightarrow T_1$ (intersystem crossing). A bimolecular process is also possible, namely excimer formation $S_1 + S_0 \longrightarrow S_1'$, where the prime denotes an excimer electronic state. The singlet excimer can then dissociate according to unimolecular processes: $S_1' \longrightarrow S_0 + S_0$ (delayed fluorescence, internal conversion), and $S_1' \longrightarrow T_1 + S_0$ (intersystem crossing).

TTA thus generates one excited singlet that yields a ground state singlet either by internal conversion or by delayed fluorescence, or reverts back into a triplet, directly by intersystem crossing or indirectly via excimer formation–dissociation. As a consequence, either zero or one triplet excitations can result from the annihilation of two triplets [19]. In systems with a high density of chromophores, triplet motion is possible not only by molecular displacement (molecular diffusion), but also by triplet-triplet energy hopping [15, 19], $T_1 + S_0 \longrightarrow S_0 + T_1$. Like TTA, this process of energy transfer is short-ranged, and takes place only between nearest-neighbors.

The aim of this work is the study of the kinetics of TTA and of the associated delayed fluorescence in nanosystems (linear chains and particles) with efficient triplet-triplet energy migration, paying special attention to the size dependence. Two formalisms for the description of TTA are presented in some detail in Secs. 2 and 3. In Sec. 4 the survival probability for an annihilating pair of triplets is introduced and a simple equation for its time-dependence in 1D systems derived. Finally, the results are summarized in Sec. 5.

## 2. STANDARD APPROACH TO TTA

The usual approach to describe TTA kinetics is based on the bimolecular rate equation, in which it is assumed that the effective annihilation rate is proportional to the density of triplet excitations. This rate equation can be written as [7, 16, 17, 19]

$$\frac{dN}{dt} = -kN - \gamma_0 N^2, \qquad (1)$$

where $N$ represents the average triplet excitation density, understood here as the number of excitations per closed domain (a linear polymer chain, micelle, nanoparticle, etc.), $k$ is the relaxation constant of triplet excitation ($1/k$ being thus the intrinsic lifetime of the triplet state), and $\gamma_0$ is the so-called annihilation constant, having the dimensions of 1/time. The solution of Eq. (1) is well known,

$$N(t) = \frac{kN_0}{ke^{kt} + \gamma_0 N_0(e^{kt} - 1)}, \qquad (2)$$

where $N_0$ is the initial number of triplet excitations in the domain.

The typical picture that one has in mind when modeling TTA according to Eq. (1) is as follows: First, it is usually assumed that, as a result of strong disorder and/or high temperature, the triplet excitations represent, in fact, molecular excitations and the rate constant $k$ has the meaning of a unimolecular decay rate. Second, it is assumed that the excitations can diffusive within the system. If the diffusion rate is large compared to the rate of nearest-neighbor annihilation, $V$, the decay is annihilation-controlled, and $\gamma_0 = V/2$. On the other hand, if $V$ dominates over the diffusion rate, the process is diffusion-influenced and the effective annihilation constant $\gamma_0$ is determined not only by the annihilation rate, but also by the pair correlation function of two excitations. In this case the annihilation rate is in general time-dependent, as was discussed in detail in several works [7, 20–25].

The above description has limitations, which can become rather important at very low temperatures. At these temperatures, triplet excitations can be delocalized over several molecules and form excitons [26, 27].

In this work, we will study the kinetics of TTA in systems where triplet excitations are strongly localized and represent molecular excitations, and where TTA is sufficiently fast so that the overall process is diffusion-influenced.

It follows from Eq. (2) that the phosphorescence intensity, normalized to unity at $t = 0$, $I_P(t) = N(t)/N_0$, can be written as a series:

$$I_P(t) = \frac{1}{1+\gamma_0 N_0/k}e^{-kt} + \frac{\gamma_0 N_0/k}{(1+\gamma_0 N_0/k)^2}e^{-2kt} + \\ + \frac{(\gamma_0 N_0/k)^2}{(1+\gamma_0 N_0/k)^3}e^{-3kt} + \dots \tag{3}$$

Analogous but truncated series, containing only two or three terms, are often used in the fitting of TTA observables like time-resolved phosphorescence or triplet-triplet absorption. Note that each term in Eq. (3) decays exponentially with time, and the respective time dependence is determined by the intrinsic relaxation constant, $k$, of triplet excitation. Only the amplitude of each term depends on the annihilation constant, $\gamma_0$.

## 3. STATISTICAL APPROACH TO TTA

A more general approach for the description of TTA is the so-called statistical approach, used by Paillotin *et al.* [28] (see also Refs. 7 and 11). In this approach, ensembles of closed domains (e.g., non-interacting polymer chains, micelles, or nanoparticles) are considered. After pulse excitation and singlet-triplet conversion, each domain contains, on the average, $N_0$ triplet excitations. Distribution of excitations over domains is given by the Poisson distribution. There are two bimolecular excitation annihilation constants, $\gamma^{(1)}$ and $\gamma^{(2)}$, corresponding to the disappearance of one or two triplets in the annihilation event. It is assumed that excitations in different domains cannot interact with each other. The overall annihilation constant is $\gamma = \gamma^{(1)} + \gamma^{(2)}$. After introducing the following parameters: $r = 2k/\gamma$ and $Z = N_0(1 + \gamma^{(2)}/\gamma)$, the phosphorescence intensity, $I_P(t)$, is given by [28]

$$I_P(t) = \sum_{p=0}^{\infty} b_{p+1}\exp[-(p+1)(p+r)\gamma t/2] = \\ = b_1 e^{-kt} + b_2 e^{-\gamma t - 2kt} + b_3 e^{-3\gamma t - 3kt} + \\ + b_4 e^{-6\gamma t - 4kt} + b_5 e^{-10\gamma t - 5kt} + \dots, \tag{4}$$

where

$$b_{p+1} = \sum_{m=0}^{\infty} \frac{(-1)^m (p+m)! Z^{p+m}(r+1+2p)}{p!m!(r+p+1)(r+p+2)\dots(r+p+1+p+m)}. \tag{5}$$

Note that parameters $b_p$ are always positive.

Both Eqs. (3) and (4) are sums of exponentials in time, however the arguments of the exponentials in Eq. (3) do not depend on the TTA constant, $\gamma$, while the arguments of the exponentials in Eq. (4) are also functions of the TTA constant.

The dependence of coefficients $b_p$ on $r$ for two different values of $Z$ (a measure of the average number of triplet excitations per domain) is shown in Fig. 1. This figure shows that the first two or three terms in Eq. (4) suffice to describe the experimental decay of phosphorescence. In general the series in Eq. (4) is rapidly convergent.

It was shown previously [28] that Eq. (4) reduces to Eq. (2) in the limit $r \longrightarrow \infty$ (i.e., $2k/\gamma \longrightarrow \infty$) by putting $Z = N_0$ and $\gamma = 2\gamma_0$. This means that Eq. (1) is valid when the rate of bimolecular annihilation is much smaller than the unimolecular decay rate.

In comparison with the standard approach, the statistical approach is valid even for domains with small dimensions and large annihilation constants, which explains the dependence on $\gamma$ of the decay constants in Eq. (4).

The form of the phosphorescence decay given by Eq. (4) has a simple interpretation. The first term corresponds to domains containing initially only one triplet, therefore they decays exponentially with the rate constant $k$. The second term reflects the disappearance of domains containing exactly two excitations. Each excitation decays individually with the rate constant $k$ and together with rate constant $\gamma$. The third term is the decay of domains containing exactly three excitations. Each excitation decays individually with the rate constant $k$ and together with rate constant $3\gamma$. The numerical coefficient 3 near $\gamma$ is the number of ways (in two or three-dimensional cases) by which three excitations can meet in pair collisions. This number is equal to number of pairs that can be formed from three elements (the binominal coefficient), $C_3^2$. The $n$th term in the series Eq. (4) is the decay of domains containing exactly $n$ excitations. Each excitation decays individually with the rate constant $k$ and together with the rate constant $C_n^2\gamma$, where $C_n^2 = n(n-1)/2$ is equal to number of pairs that can be formed from $n$ elements.

The correctness of this interpretation is supported by the following simple scheme: Let $N_1(t)$, $N_2(t)$, and $N_3(t)$ be the numbers of domains containing at time $t$ exactly one, two, and three excitations, respectively. Assume, for simplicity, that TTA always converts two triplets into one triplet. In this case, and owing to TTA and unimolecular decay, domains with three excitations become domains with two excitations and domains with two excitations become domains with one excitation. Hence, the following set of rate equations can be written:

$$\frac{d}{dt}N_1 = -kN_1 + (\gamma + 2k)N_2, \tag{6a}$$

$$\frac{d}{dt}N_2 = -(\gamma + 2k)N_2 + (3\gamma + 3k)N_3, \tag{6b}$$

$$\frac{d}{dt}N_3 = -(3\gamma + 3k)N_3. \tag{6c}$$

The solution of these equations is

$$N_3(t) = N_3(0)e^{-(3\gamma + 3k)t}, \tag{7a}$$

$$\begin{aligned} N_2(t) = {} & \left(N_2(0) + \frac{3\gamma + 3k}{2\gamma + k}N_3(0)\right)e^{-(\gamma + 2k)t} - \\ & - \frac{3\gamma + 3k}{2\gamma + k}N_3(0)e^{-(3\gamma + 3k)t}, \end{aligned} \tag{7b}$$

$$\begin{aligned} N_1(t) = {} & \left(N_1(0) + \frac{\gamma + 2k}{\gamma + k}N_2(0) + \right. \\ & \left. + \frac{(\gamma + 2k)(3\gamma + 3k)}{(\gamma + k)(3\gamma + 2k)}N_3(0)\right)e^{-kt} - \\ & - \frac{\gamma + 2k}{\gamma + k}\left(N_2(0) + \frac{3\gamma + 3k}{2\gamma + k}N_3(0)\right)e^{-(\gamma + 2k)t} + \\ & + \frac{(\gamma + 2k)(3\gamma + 3k)}{(3\gamma + 2k)(2\gamma + k)}N_3(0)e^{-(3\gamma + 3k)t}. \end{aligned} \tag{7c}$$

The total number of excitations, $N(t)$, is

$$N(t) = N_1(t) + 2N_2(t) + 3N_3(t) \tag{8}$$

and can be written as a series

$$N(t) = C_1e^{-kt} + C_2e^{-(\gamma + 2k)t} + C_3e^{-(3\gamma + 3k)t}. \tag{9}$$

The coefficients $C_i$ depend on rate constants $\gamma$ and $k$ and on the initial number of domains, $N_1(0)$, $N_2(0)$, $N_3(0)$, but not on time.

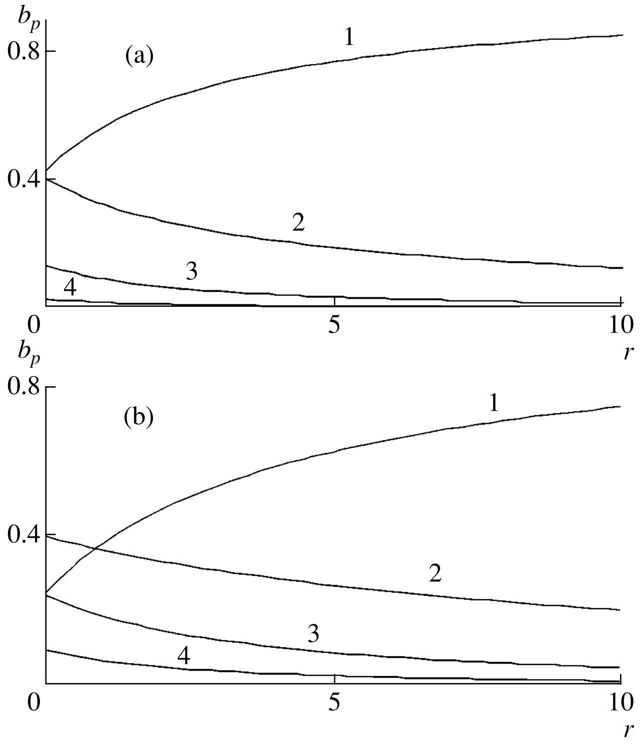

**Fig. 1.** Dependence of coefficients $b_p$ on $r$ for two different values of $Z$ (proportional to the average number of triplet excitations per domain): $Z = 2$ (a) and $Z = 4$ (b). Numbers next to the curves are values of $p$.

It follows from the comparison of Eqs. (9) and (4) that the time dependent multipliers in Eq. (4) reflect the kinetics of disappearance of domains containing exactly one, two, three, and so on excitations, respectively.

Like the standard approach, the statistical approach does not give any information on how the annihilation constant in a domain (polymer chain, nanoparticle, etc.) depends on the rate of excitation diffusion (i.e., the frequency of hops between nearest-neighbor chromophores in the domain, $W$), on the rate of nearest-neighbor annihilation, $V$, and on the size (for example, the number of segments, $M$, in the polymer chain) and dimension of the domain. To our knowledge, the first and single attempt to answer some of these questions was done in [29], for the case of a one-dimensional lattice and $V = \infty$.

## 4. SURVIVAL PROBABILITY FOR AN ANNIHILATING PAIR OF TRIPLETS

The survival probability for an annihilating pair of triplets, $\rho_M^{(2)}(t)$, diffusing in one-dimensional structures

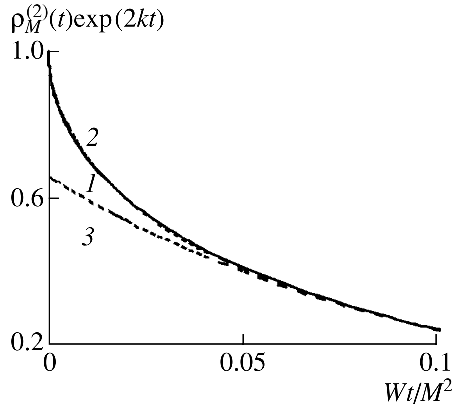

**Fig. 2.** Survival probability for an annihilating pair of excitations in a linear lattice, $\rho_M^{(2)}(t)$, for $V/W = \infty$. Exact solution Eq. (10) (solid line *1*) and approximations: Dotted lines *2* and *3* are the approximate decay function Eq. (13) and the long time asymptote Eq. (11), respectively.

(e.g., a polymer chain with $M$ chromophores) was calculated in Ref. 29. It was assumed that the excitation jumps between neighboring lattice sites with a unit time probability $W$; when two excitations meet at the same site they immediately annihilate, i.e., the annihilation rate is infinite, $V = \infty$. Solution of the master equation for uniform initial excitation in a one-dimensional lattice (a chain), with $M \gg 1$, and $Wt \gg 1$ is

$$\rho_M^{(2)}(t) = \exp(-2kt)\frac{2^6}{\pi^4}\times \left\{\sum_{l=1}^{\infty}\frac{1}{(2l-1)^4}\exp\left(-(2l-1)^2\frac{\pi^2 Wt}{M^2}\right) + 2\sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\frac{1}{((2m)^2-(2l-1)^2)^2}\times \exp\left(-((2m)^2+(2l-1)^2)\frac{\pi^2 Wt}{M^2}\right)\right\}. \qquad (10)$$

Note the important fact that Eq. (10) depends on the combination of parameters $Wt/M^2$.

The asymptotes of the survival probability at short and long times are

$$\rho_M^{(2)}(t) = \exp(-2kt)\begin{cases} 1 - \dfrac{4\sqrt{2}}{\sqrt{\pi}}\sqrt{\dfrac{Wt}{M^2}}, & \dfrac{Wt}{M^2} \ll 1, \\ \dfrac{2^6}{\pi^4}\exp\left(-\pi^2\dfrac{Wt}{M^2}\right), & \dfrac{Wt}{M^2} \gg 1. \end{cases} \qquad (11)$$

The long time asymptote can be obtained from simple considerations. On the average, each of two excitations can freely move in half of the chain, whose size is $M/2$. After collision in the middle of the chain, one or two excitations disappear. Therefore, to a first approximation, the motion of every excitation is equivalent to motion along a chain of length $M/2$ that contains a quencher at one end. The rate of excitation quenching at this end is infinite, $V = \infty$. The kinetics of excitation decay in this case was previously obtained [30] and its long time asymptote for large $M$ is $(8/\pi^2)\exp(-\pi^2 Wt/M^2)$. This asymptote coincides with asymptote Eq. (11) to a numerical coefficient.

Based on the interpretation of series Eq. (4), and comparing the long time asymptote Eq. (11) with the second term of series Eq. (4), we obtain the dependence of the annihilation rate constant, $\gamma$, on the unit time probability of jump between nearest-neighbor sites, $W$, and on the size of a one-dimensional lattice (a chain), $M$,

$$\gamma = \pi^2 W/M^2. \qquad (12)$$

Indeed, the annihilation rate constant should decrease as the size of the domain increases.

After careful numerical calculations of Eq. (10) and taking into account the asymptotes (11), we obtained the approximate equation for $\rho_M^{(2)}(t)$,

$$\rho_M^{(2)}(t) = \exp(-2kt)\left\{\left(1-\frac{2^6}{\pi^4}\right)\times \exp\left[-\frac{4\sqrt{2}}{(1-2^6/\pi^4)\sqrt{\pi}}\sqrt{\frac{Wt}{M^2}} - \left(30\frac{Wt}{M^2}\right)^{3/2}\right] + \frac{2^6}{\pi^4}\exp\left[-\pi^2\frac{Wt}{M^2}\right]\right\}, \qquad (13)$$

which reproduces the exact solution (10) with high precision (better 2%) at all times (see Fig. 2). Equation (13) gives the correct time dependence of the second term in Eq. (4). The higher terms in Eq. (13) decrease faster, first two terms suffice to describe the experimental decay of phosphorescence.

## 5. CONCLUSION

In this paper, triplet-triplet annihilation was studied. In particular, the dependence of annihilation rate constant on nanoparticle size, $M$, on the rate of excitation migration, $W$, and on the rate of excitation annihilation, $V$, was obtained in 1D systems.

We showed that the usual TTA observables (phosphorescence, triplet-triplet absorption), are well described by a sum of two exponentials. The first term describes the decay of domains containing exactly one excitation, while the second one reflects the disappearance of domains containing exactly two excitations. The higher terms of the infinite series expansion, describing domains containing three or more excitations, decay much faster and can be omitted (especially in the case of relatively low intensity excitation).

In Sect. 4, the diffusion-influenced limit ($V \gg W$) was considered where the rate of nearest-neighbor annihilation, $V$, dominates over the diffusion rate, $W$. In the opposite case (annihilation-controlled limit, $W \gg V$), the diffusion rate is large compared to the rate of nearest-neighbor annihilation, and the distribution of excitations over the domains is homogeneous (diffusion displacement of triplet excitation during the lifetime, $\sqrt{D/k}$, large compared to the size of the domains, $Ma$, i.e., $\sqrt{W/k} > M$; here $D$ is diffusion constant, $D \approx Wa^2$, and $a$ is a distance between heighboring lattice sites). The statistical approach is in such a case valid, $\gamma = V$ and Eq. (4) applies.

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